474. *A New Apparatus for Studying the Evaporation of Water Through Monolayers.*

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An apparatus has been developed for investigating the effect of mono-layers on the rate of evaporation of water into an atmosphere at low pressure. The technique, which has proved more sensitive than earlier methods, has revealed that the critical surface pressure at which the resistance to evaporation of stearic acid first becomes appreciable is very close to the surface pressure at which the film becomes relatively incompressible. On the other hand, a film of cholesterol, though it becomes incompressible at very low surface pressures, does not affect the rate of evaporation of the substrate.

Sebba and Briscoe (*J.*, 1940, 106) reported an investigation into the effect of monolayers, spread on a water substrate, on the rate of evaporation of the water. They allowed the water to evaporate into a stream of initially dried air passed over the surface under controlled conditions. This method, though satisfactory for comparative purposes, did not lend itself to determination of absolute measurements of rates of evaporation. A simpler technique was used by Langmuir and Schaefer (*J. Franklin Inst.*, 1943, **235**, 119) who supported a drying agent just above the water surface and measured its increase in weight. Since both methods entailed evaporation into air at atmospheric pressure, they might have obscured effects which would be revealed if the rate of evaporation were increased by use of a partial vacuum.

Rideal (*J. Phys. Chem.*, 1925, **29**, 1585) found that the rate of evaporation of water in a vacuum from one leg of an inverted U-tube at 25° into the other leg at 0° was reduced by 28% by stearic acid held at its equilibrium pressure. Unfortunately this technique does not lend itself to control of the surface pressure of the monolayer, a factor that Sebba and Briscoe showed to be of critical importance. An apparatus was, therefore, designed to study the rate of evaporation into an atmosphere at low pressure, while at the same time enabling the surface pressure to be controlled and recorded.

EXPERIMENTAL

The apparatus (Fig. 1) consisted of a steel vacuum-chamber 36 × 18 × 18", with a removable face that could be bolted on to give an air-tight box and had a " Perspex " window 12 × 12 × ¾" supported by two steel struts 1" wide and 3" apart, as well as a removable steel door 12 × 12 × ¼". This door, supported by a frame ½" wide, could be sealed in position with plasticine. A was a small glass window 2 × 6 × ½" through which a beam of light was focused on to a mirror B, attached to the arm of the surface balance C of the Wilhelmy type (Harkins and

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Anderson, *J. Amer. Chem. Soc.*, 1937, **59**, 2189). The reflected beam emerged through the same window on to a scale *D*, situated 1 m. from the balance.

A copper tube *E*, 1″ in diameter, closed at the bottom and passing through the top of the chamber, was held a few cm. above the water surface by means of a rubber disc which formed a seal as soon as the pressure inside the box was reduced. It was cooled by being filled with solid carbon dioxide–alcohol and the water which had evaporated condensed on its outer surface *F*. *G* provided access to the pumping unit through traps, and *H* access to a manometer. Once the vapour had condensed on the freezing-tube, air could be admitted quickly into the chamber through tap *I*.

The Langmuir–Adam trough *J* stood in a larger tray *K*, which collected any water which overflowed during the sweeping of the surface. In order to control the area from which evaporation was being measured, a glass slab *N* was supported 1 mm. above the water surface. It was always moved close up behind the chromium-plated barrier used to control the surface pressure of the film. The temperature of the water was kept at 20° by circulation of water from a thermostat at 24° through the glass coil *P*.

FIG. 1.
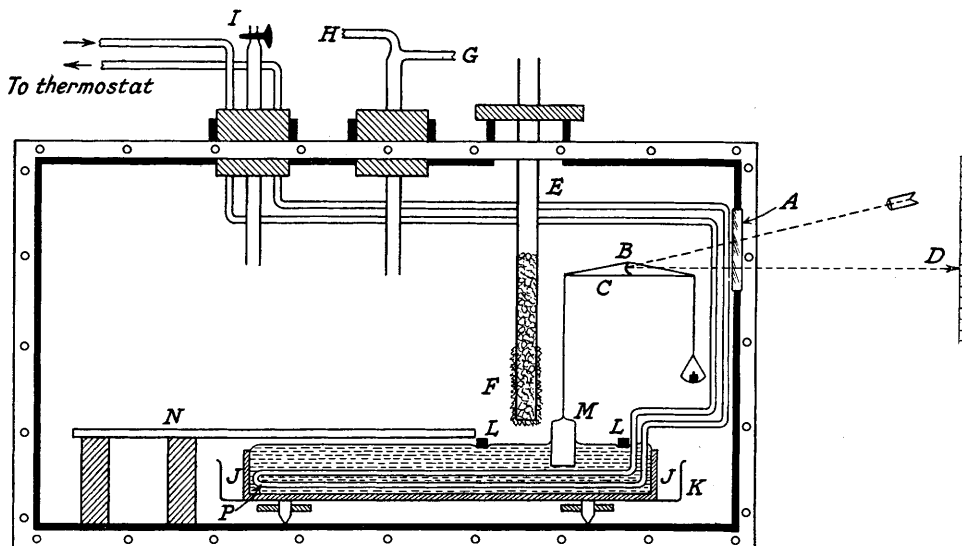
The final pressure in the chamber should be as low as possible but was limited by the vapour pressure of water, since if the water boiled freely in the trough, the film would be disrupted. On the other hand if the pressure was too high, the convection currents produced when the tube *E* was cooled froze the water directly under the tube. A pressure of 35 mm. was low enough to reduce convection effects to negligible dimensions. Evacuation took approximately 90 minutes.

When the desired pressure had been reached, the pump was disconnected and the freezing-mixture was poured into the tube *E*. Water vapour was allowed to freeze on the cold tube for a determined time (270 seconds) and then air was let into the chamber as rapidly as possible (30 seconds). This decreased the rate of condensation of the water and, as the experiments were carried out under strictly standardised conditions, the error introduced by letting in the air was minimised. The copper tube with its adherent deposit of snow was transferred to an apparatus where the weight of the condensed water was determined by distilling the deposit under reduced pressure into a tared trap ($-80°$) and a guard tube containing anhydrone. Approx. 4—5 g. of water were collected.

The amounts of water evaporated in 300 seconds at 35 mm. from a clean water surface were determined with the glass slab *N* exposing various areas of the water surface. Plotting the weight of water collected against the area of surface exposed gave a straight line (Fig. 2). If no water surface was exposed, 3·12 g. of water were condensed; this corresponds to the saturation vapour content of the chamber, being the amount of water vapour present in the chamber at the

instant when the freezing mixture was poured into the copper tube, and it was condensed in addition to the water which subsequently evaporated. In estimations of the amount of evaporation from the surface, this weight of water had to be subtracted from the total weight of water collected.

RESULTS

The choice of a suitable film-forming substance revealed the defect of the apparatus in its original dimensions, since owing to the solubility of the film in the water substrate (Sebba and Briscoe, *J.*, 1940, 114) there are few monolayers which can be kept at a constant surface pressure for 90 minutes, the time required for the evacuation of the chamber. However, stearic acid has some measure of stability (a pure sample prepared by the hydro-
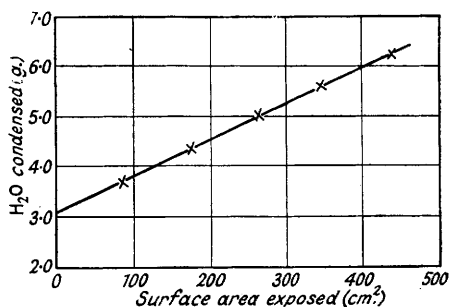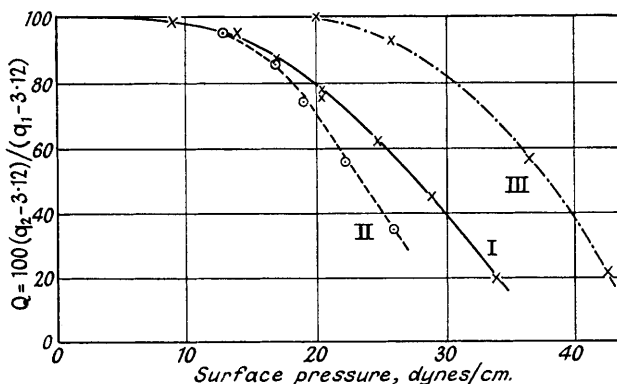
FIG. 2.

FIG. 3.

genation of oleic acid was kindly presented by Dr. H. M. Schwartz of the South African C.S.I.R.). This was spread from solution in benzene (shown to be completely free from surface-active contaminants).

Two series of experiments were made. In one case, the substrate was a buffer of pH 7 (1·1 g. of borax and 11·6 g. of boric acid per l.), in the second it was 0·01N-hydrochloric acid. The film was much less soluble, and maintained a steady surface pressure on the latter substrate.

The surface pressure recorded was that at the time of condensation of the water vapour. By return to the trough of all the water which had condensed in the traps during the evacuation of the chamber, the surface pressure was corrected for the decrease in the level of the water in the trough. As the Wilhelmy type of surface balance is very sensitive to changes of contact angle, the angle was visually examined to ensure it was zero (a small light inside the box enabled a change in contact angle to be observed; it usually only occurred at high surface pressures, and was due to the build-up of films on the glass slide).

If the weight of water collected in a given time with a film on the surface was q_2, then $(q_2 - 3 \cdot 12)$ was the true weight evaporated (cf. above). Similarly, q_1, the quantity of water evaporated in the same time from the same area of a clean water surface was obtained from the graph (Fig. 2) and the corrected weight was $(q_1 - 3 \cdot 12)$. The value $Q = 100(q_2 - 3 \cdot 12)/(q_1 - 3 \cdot 12)$ was determined at different surface pressures.

Fig. 3 shows the variation of Q with surface pressure for stearic acid, (I) on buffer of pH 7 and (II) on $0 \cdot 01$N-HCl, and (III) (for comparison) the curve obtained by Sebba and Briscoe (*loc. cit.*). Too much significance should not be attached to the difference between (I) and (II) at the higher surface pressures. This may, in part, be explained by the fact that in case (I) the stearic acid film was gradually dissolving and, therefore, the surface pressure recorded may have been a few dynes higher than the true surface pressure. This is due to the inherent weakness of the Wilhelmy balance, that though it records accurately when the contact angle is receding, *i.e.*, if the surface pressure is being increased, it is unreliable when the contact angle is advancing. What is significant is the difference between these curves and curve (III), because a small but definite lowering of Q, even at low surface pressures, is observable. This was not observed by Sebba and Briscoe and is an indication of increased sensitivity of the new technique.

There is a marked change in evaporation resistance at a surface pressure of about 15 dynes/cm., and at almost the same point in curves (I) and (II). This is approx. the surface pressure at which the stearic acid becomes relatively incompressible. Sebba and Briscoe pointed out that their stearic acid first showed marked evaporation resistance at a surface pressure significantly in excess of the pressure at which the stearic acid becomes incompressible. They were unable to explain this, but it was probably due to lack of sensitivity of their method. It now appears that the point of incompressibility is closely related to increased evaporation resistance.

Rideal found that a film of stearic acid at its equilibrium pressure reduced the rate of evaporation of water into a vacuum by 28·1%. The equilibrium pressure of stearic acid is 20 dynes/cm. and it will be seen from Fig. 3 that at a surface pressure of 20 dynes/cm., Q is 78%, corresponding to a 22% reduction, in reasonable agreement with Rideal's results which were obtained at 25°.

The apparatus was used to resolve a controversy regarding films of cholesterol. Langmuir and Schaefer (*J. Franklin Inst.*, 1943, **235**, 119) found that monolayers of cholesterol decreased the rate of evaporation of water by about 30%, even at surface pressures considerably lower than the equilibrium pressure (38 dynes/cm.). On the other hand, Sebba and Briscoe could not detect such retardation, even at pressures of 35 dynes/cm. By using our more sensitive technique, it was found that a film of cholesterol at its equilibrium pressure did not produce any detectable retardation of evaporation, in spite of the fact that cholesterol gives a condensed film. This indicates that incompressibility is not the only factor in determining the effect of films on the rate of evaporation.